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(54) **PROCESS FOR PRODUCING SODIUM BICARBONATE**

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CPC .. **C22B 26/10** (2013.01); **C01D 7/10** (2013.01)

(58) **Field of Classification Search**
None
See application file for complete search history.

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(57) **ABSTRACT**

A process for producing sodium bicarbonate from a sodium carbonate bearing stream (A) comprising at least 2% sodium chloride and/or sodium sulfate by weight, a part of such stream (A) being generated by a sodium carbonate crystallizer, comprising: a) mixing the stream (A) with part of a stream (B) to produce a stream (C); b) bicarbonating the stream (C) with a gas (D) comprising CO₂ to produce an aqueous suspension (E) containing crystals (F) comprising sodium bicarbonate crystals; c) separating the aqueous suspension (E) to obtain crystals (F) comprising sodium bicarbonate crystals and an aqueous mother liquor (G); d) partly debicarbonating such liquor (G) and removing part of the water to obtain the stream (B) and an optional gas (H); e) recycling at least part of the stream (B) to step a); and f) removing the remainder of the stream (B) or part of the aqueous mother liquor (G) to be further processed.

20 Claims, 2 Drawing Sheets

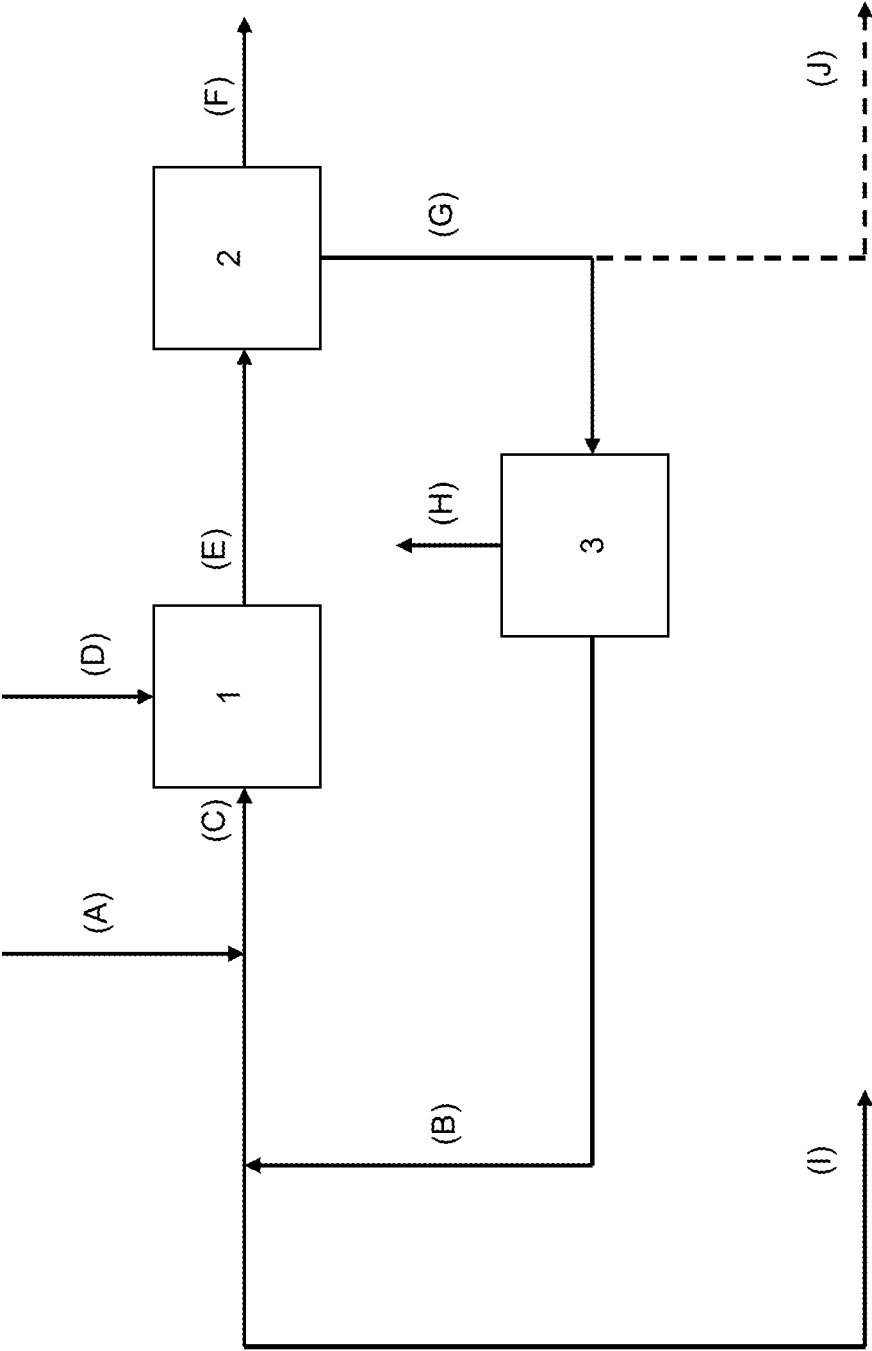


Fig. 1

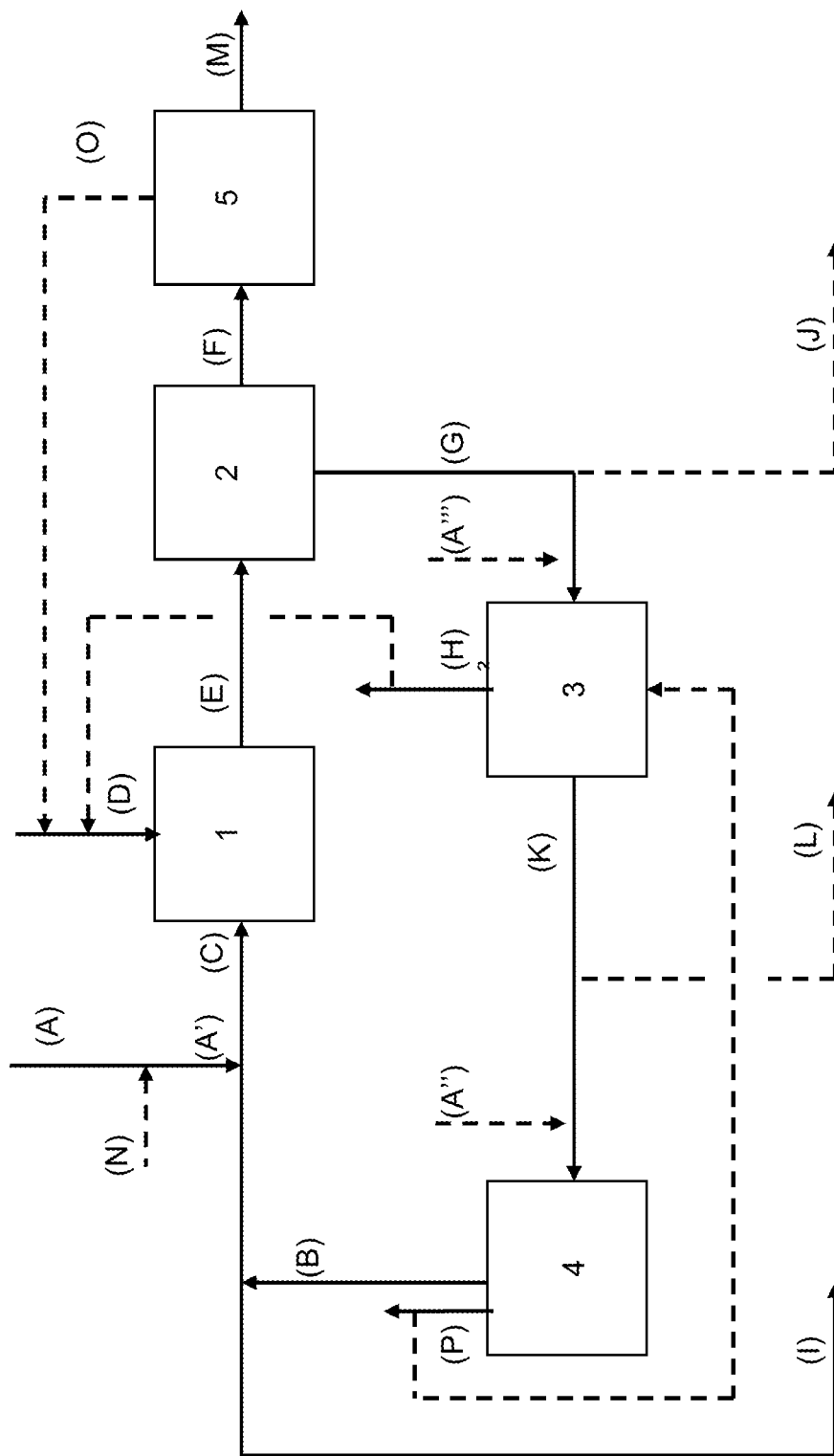


Fig. 2

PROCESS FOR PRODUCING SODIUM BICARBONATE

CROSS-REFERENCE TO RELATED APPLICATIONS

This application claims priority to U.S. provisional application Nos. 61/578,160 and 61/578,162, both filed on Dec. 20, 2011, the whole content of each of these applications being incorporated herein by reference for all purposes.

TECHNICAL FIELD OF THE INVENTION

The invention relates to a process for producing sodium bicarbonate from a sodium carbonate bearing stream, a part of which is generated by a sodium carbonate crystallizer, such sodium carbonate bearing stream comprising sodium carbonate and a water-soluble impurity, while minimizing a final volume of a purge necessary when producing the sodium carbonate, and also minimizing the loss of sodium carbonate associated with such purge.

BACKGROUND OF THE INVENTION

Sodium carbonate (Na_2CO_3), or soda ash, is one of the largest volume alkali commodities made world wide with a total production in 2008 of 48 million tons. Sodium carbonate finds major use in the glass, chemicals, detergents industries, and also in the sodium bicarbonate production industry. The main processes for sodium carbonate production are the Solvay ammonia synthetic process, the ammonium chloride process, and the trona-based processes.

Trona ore is a mineral that contains up to 99% sodium sesquicarbonate ($\text{Na}_2\text{CO}_3 \cdot \text{NaHCO}_3 \cdot 2\text{H}_2\text{O}$). Trona-based soda ash is obtained from trona ore deposits in Green River (Wyo.), Turkey, China, and Kenya either by conventional underground mining techniques, by solution mining or lake waters processing. The trona-based sodium carbonate from Wyoming comprised about 90% of the total U.S. soda ash production.

A typical analysis of the trona ore in Green River is as follows:

TABLE 1

Constituent	Weight Percent
Na_2CO_3	43.4
NaHCO_3	34.4
H_2O (crystalline and free moisture)	15.4
NaCl	0.01
Na_2SO_4	0.01
Fe_2O_3	0.14
Insolubles	6.3
Organics	0.3

Trona deposits contain highly diverse soluble impurities such as alkaline metal halides (sodium chloride, potassium chloride, sodium fluoride, . . .), alkaline metal sulfates (sodium sulfate, potassium sulfate, . . .), alkaline metal nitrate (sodium nitrate, potassium nitrate, . . .), alkaline metal borate, alkaline metal phosphates, etc. . . . Those highly soluble impurities are in various proportions depending on the geographic location of the deposits. In particular, sodium chloride and sodium sulfate may represent several percents or several tens percents of trona ore depending on the geographic location.

Trona deposits also include slightly soluble mineral or organic impurities. Examples of slightly soluble mineral are:

alkali metal and alkali earth metal silicates, aluminates, titanates, vanadates, metallic compounds and salts. The organic impurities come from organic sediments that were captured during the formation of the deposits and that frequently have formed oil shales during geological aging. Both mineral and organic soluble impurities may also be partially generated during the trona processing in the mine or on surface operations. In particular thermal treatments, such as calcination, generally amplify the quantity of some soluble impurities such as sodium silicates, and sodium salts of organic compounds by thermal saponification.

Other "insoluble" or very slightly water-soluble mineral impurities found in trona or adjacent to trona deposits are generally mixtures of different minerals, the most frequent of which are calcite, dolomite, pirssonite, zeolite, feldspar, clay minerals, iron/aluminium silicates, and calcium sulfate.

Two main techniques well known in the art are used to recover trona ore from trona ore deposits. The first technique is a mechanical mining, also called conventional mining, such as a room and pillar panel operation or a longwall operation. The second technique is a solution mining recovering wherein trona is dissolved with water and recovered as a solution.

Among the several ways in which sodium carbonate can be recovered from trona ore that contains other salts and impurities, the most widely practiced is the so called "monohydrate process". In that process a mined trona ore is crushed, then calcined into crude sodium carbonate, then leached with water, the resulting water solution is purified and fed to a crystallizer where pure sodium carbonate monohydrate crystals are crystallized. The monohydrate crystals are separated from the mother liquor and then dried into anhydrous sodium carbonate. Most of the mother liquor is recycled into the crystallizer. However, the soluble impurities contained in the trona ore, tend to accumulate into the crystallizer. To avoid build up of impurities, the mother liquor must be purged. The purge liquor, which represents important quantities for industrial monohydrate plants, is commonly sent to an evaporative pond, also called tailings pond. The significant quantity of alkali which is contained in the purge liquor is consequently lost. Moreover, the stocking of large quantities of purge liquors in evaporative ponds raise environmental problems, because of the scarce availability of new areas for stocking.

Variants to produce sodium carbonate from trona ore, in particular when solution mining is used, is:

either crystallizing refined sodium sesquicarbonate (sesqui) after evaporation of water, then calcining the sodium sesqui into soda ash;

or alternatively decomposing thermally (with steam) or calcine chemically (with caustic soda) the dissolved sodium bicarbonate to transform it into dissolved sodium carbonate, then evaporating the water in order to crystallize pure sodium carbonate monohydrate.

In those variants, the soluble impurities contained in the trona ore, tend to accumulate also into the sesqui or the monohydrate crystallizers. To avoid the build up of impurities, the mother liquors must also be purged, raising the same environmental problems in evaporative ponds as the monohydrate process.

Sodium bicarbonate (NaHCO_3), aside sodium carbonate, is another important alkali product with a wide range of applications including human food, animal feed, flue gas treatment, and chemical industries. The production of sodium bicarbonate is currently almost entirely made by the carbonation of solid or aqueous solutions of sodium carbonate with gaseous CO_2 either produced in situ in the soda ash plants or purchased independently.

Several technical alternatives have been proposed to reduce the purge volume from soda ash plants.

US2003/0143149 discloses a process for recovering sodium-based chemicals from sodium carbonate streams such as recycle, purge, and waste streams from sodium carbonate crystallizers, mine water, evaporative pond water and sodium carbonate decahydrate deposits. The sodium bicarbonate from those streams is partially destroyed by a decarbonization and the resulting stream is fed mainly back to a sodium carbonate monohydrate crystallizer, and the remainder of the resulting decarbonized stream is fed to a sodium carbonate decahydrate crystallizer, from which purified decahydrate is recovered and recycled to monohydrate crystallizer and a purge concentrated in impurity such as sodium sulfate is disposed off. Although the purge reduction factor of this process is limited, because, when high concentration of impurities is reached, sodium carbonate and sodium sulfate form decahydrated mixed salts. And if high amounts of sodium sulfate are recycled back to carbonate monohydrate crystallizer, they generate burkeite crystals ($\text{Na}_2\text{CO}_3 \cdot 2\text{Na}_2\text{SO}_4$) that are detrimental to sodium carbonate monohydrate quality.

US2004/0057892 discloses a process for the production of sodium carbonate and bicarbonate, according to a purge liquor from a monohydrate sodium carbonate crystallizer is introduced into a sodium carbonate decahydrate crystallizer and the purified decahydrate crystals are converted into sodium bicarbonate. It has been observed that this process is not efficient when the purge liquor, depending on the trona source, contains high levels of impurities. High levels of sodium chloride in the purge liquor prevent smooth crystallization of sodium carbonate decahydrate.

U.S. Pat. No. 2,926,995 discloses a process for producing sodium bicarbonate crystals from sodium carbonate solutions containing sodium chloride from electrolytic caustic soda-chlorine cells.

U.S. Pat. No. 7,507,388 discloses a process for the production of sodium carbonate and bicarbonate, from a pre-purified solution comprising bicarbonate which is first partially decarbonized and then used in both a sodium bicarbonate line and a sodium carbonate monohydrate line. The purge stream of the sodium carbonate monohydrate crystallizer is either sent into a mixed sodium carbonate decahydrate and sodium sesquicarbonate line wherein resulting filtrate is discarded as the final purge of the process or sent after dilution into a light soda ash line comprising an intermediate sodium bicarbonate carbonation step, the bicarbonate is separated from the filtrate, and this filtrate is also disposed as a final purge. The total amounts of generated purges is very high (1.28 t of purges per ton of dense soda ash) and corresponds to 6 to 15 weight percents of purged sodium carbonate per ton of produced dense soda ash.

US2009/0291038 (Solvay) discloses a process for the joint production of sodium carbonate and sodium bicarbonate crystals, according to which a solid powder derived from sodium sesquicarbonate such as calcined trona is dissolved in water, the resulting water solution is introduced into a crystallizer, wherein sodium carbonate crystals and a mother liquor are produced, part of the mother liquor is taken out of the crystallizer (purge of the sodium carbonate crystallizer) and is carbonized (carbonated) to produce valuable sodium bicarbonate crystals and a second mother liquor, the second mother liquor is optionally decarbonized (debicarbonated) and then sent to a storage pond. In this document, it is taught that the mother liquor used for sodium bicarbonate crystallization should contain preferably at least 175 g/kg of sodium carbonate and not more than 60 g/kg of sodium chloride, and

not more than 20 g/kg of sodium sulfate. Consequently, the purge level of sodium alkali (carbonate or bicarbonate) sent to a pond is reduced compared to a decahydrate treatment of the purge but is still important and represents important volumes sent into ponds.

US2011/112298 discloses a method for extending the life of tailings ponds produced from purge streams containing sodium carbonate wherein the purge stream is treated with gaseous carbon dioxide, similar to the US2009/0291038 process, to produce sodium bicarbonate or sodium sesquicarbonate before being introduced in the pond. The produced sodium bicarbonate may be recovered before the introduction of the treated purge stream into tailings pond or recovered after its deposition into the pond. The document is silent on further valorizing the obtained aqueous purge when sodium bicarbonate is recovered.

However, there is still a need in the sodium carbonate and bicarbonate industry, taking into account sustainable development, to be able to further reduce the purge volume and reducing the loss of alkali in a simple way, without impairing operation conditions of the linked processes.

SUMMARY OF THE INVENTION

Accordingly, the invention concerns a process for producing sodium bicarbonate from a sodium carbonate bearing stream (A) part of it generated by a sodium carbonate crystallizer, said sodium carbonate bearing stream (A) comprising sodium carbonate and at least 2%, advantageously at least 3%, more advantageously at least 4% sodium chloride and/or sodium sulfate by weight, which comprises the following steps:

- mixing the sodium carbonate bearing stream (A) with at least a part of a stream (B) to produce a stream (C),
- bicarbonating the stream (C) with a gas (D) comprising CO_2 to produce an aqueous suspension (E) comprising crystals (F), said crystals (F) comprising sodium bicarbonate crystals,
- separating the aqueous suspension (E) in order to obtain crystals (F) comprising sodium bicarbonate crystals on the one hand and an aqueous mother liquor (G) on the other hand,
- partly debicarbonating the aqueous mother liquor (G) and removing part of the water to obtain the stream (B) and an optional gas (H),
- recycling at least a part of the stream (B) to step a), and
- removing the remainder (I) of the stream (B) or a part (J) of the aqueous mother liquor (G) to be further processed.

A first advantage of the present invention is that it reduces considerably the amount of alkali loss in the evaporative (or tailings) ponds in a smooth and inexpensive way, thanks to the synergy of the bicarbonating step d) with the partly debicarbonating step b) and with the recycling step (e) through controlling the concentration of impurities of water-soluble salt of alkaline metal in the remainder (I) of the stream (B).

A second advantage of present invention is that it is efficient on a large spectrum of soluble impurities and a large range of impurities concentrations.

A third advantage of the present invention linked to the second advantage is that it enables to exploit one or several trona deposits with different levels of soluble impurities while being able to treat the varying levels of the purges of a soda ash or a sodium bicarbonate plant with the same process described in the present invention.

A fourth advantage of the present invention is that it enables to minimize the purge flow preparing the process for

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either dry-cooking the purge or for very small evaporative ponds or for reinjecting the purge into mined out cavities.

A fifth advantage of the present invention is that it enables to reduce water consumption for soda ash production and/or sodium bicarbonate production in recovering it as condensates from evaporators for either recycle it to a calcined trona leaching or to a trona solution mining.

A sixth advantage of the present invention is that it enables to increase the production of valuable technical sodium bicarbonate from sodium alkaline streams comprising impurities.

A seventh advantage of the present invention is that the obtained technical sodium bicarbonate contains less water-soluble impurities that the sodium carbonate that would have been produced in equivalent conditions of water-soluble impurities concentration.

An eighth advantage of the present invention is that the obtained technical sodium bicarbonate is well suited for specific uses such as flue gas mitigation despite high impurities concentration.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 is a flow diagram which schematically illustrates the process of the present invention.

FIG. 2 is a flow diagram of a process according to an embodiment of the present invention.

The reference figures and letters quoted below refer to the attached drawings.

DEFINITIONS

For purposes of the present description, certain terms are intended to have the following meanings.

The term "purge" refers to a stream withdrawn from a part of a process to limit impurity concentration in this process.

The term "impurity" refers to a compound different from the sodium carbonate and/or the sodium bicarbonate to be produced.

The term "solubility" refers to the water solubility of a compound in an aqueous solution.

The term "carbonating" refers to the action of increasing the amount of total carbonate (carbonate and bicarbonate) of a stream.

The term "decarbonating" refers to the action of decreasing the amount of total carbonate (carbonate and bicarbonate) of a stream.

The term "bicarbonating" refers to the action of increasing the amount of bicarbonate of a stream.

The term "debicarbonating" refers to the action of decreasing the amount of bicarbonate of a stream.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

The present invention relates to a process for producing sodium bicarbonate from a sodium carbonate bearing stream (A), a part of which is generated by a sodium carbonate crystallizer, said sodium carbonate bearing stream (A) comprising sodium carbonate and at least 2%, advantageously at least 3%, more advantageously at least 4% sodium chloride and/or sodium sulfate by weight, which comprises the following steps:

- a) mixing the sodium carbonate bearing stream (A) with at least a part of a stream (B) to produce a stream (C),
- b) bicarbonating the stream (C) with a gas (D) comprising CO₂ to produce an aqueous suspension (E) comprising crystals (F), said crystals (F) comprising sodium bicarbonate crystals,

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c) separating the aqueous suspension (E) in order to obtain crystals (F) comprising sodium bicarbonate crystals on the one hand and an aqueous mother liquor (G) on the other hand,

5 d) partly debicarbonating the aqueous mother liquor (G) and removing part of the water to obtain the stream (B) and an optional gas (H),

e) recycling at least part of the stream (B) to step a), and

10 f) removing the remainder (I) of the stream (B) or part (J) of the aqueous mother liquor (G) to be further processed.

The present invention relates also to a process for the joint production of sodium carbonate and bicarbonate crystals comprising in a first step introducing a sodium carbonate solution comprising sodium carbonate and at least one impurity consisting of sodium chloride and/or sodium sulfate into a sodium carbonate crystallizer, producing a first aqueous suspension comprising sodium carbonate crystals, subjecting the first aqueous suspension to a separation, in order to obtain crystals comprising sodium carbonate on the one hand, which are valorized, and a mother liquor on the other hand, part of the mother liquor is taken out of the sodium carbonate crystallizer to constitute the sodium carbonate bearing stream (A) to be further processed according the present invention into crystals (F) comprising sodium bicarbonate crystals.

25 In the present invention, the sodium carbonate crystallizer means a crystallizer wherein crystals comprising sodium carbonate are generated. The sodium carbonate crystallizer is selected from the group consisting of: an anhydrous sodium carbonate crystallizer, a monohydrate sodium carbonate crystallizer, a heptahydrate sodium carbonate crystallizer, a decahydrate sodium carbonate crystallizer, a sodium sesquicarbonate crystallizer, a wegscheiderite crystallizer (wagscheiderite being Na₂CO₃·3NaHCO₃ and also called decemite), and any combination thereof. In the present invention, the sodium carbonate crystallizer may also be a container or an evaporative or tailings pond wherein crystals comprising sodium carbonate compounds are formed.

Advantageously, the sodium carbonate crystallizer is a sodium carbonate monohydrate crystallizer or a sodium sesquicarbonate crystallizer. More advantageously, the sodium carbonate crystallizer is a sodium carbonate monohydrate crystallizer.

30 The sodium carbonate bearing stream (A) may be any stream made of a solid, a suspension of a solid in an aqueous solution, or an aqueous solution comprising sodium carbonate, and suitable for feeding a sodium bicarbonate crystallizer.

The sodium carbonate bearing stream (A) may derive partly or totally from trona or nahcolite. Preferably, the sodium carbonate bearing stream (A) derives partly or totally from trona. In the present invention, the trona is generally processed by conventional mining. Advantageously, the trona may be also processed by solution mining.

55 The sodium carbonate bearing stream (A) may also derive, in part or in its entirety, from tailings pond solids comprising sodium carbonate. This may be of particular advantage if the considered tailings pond solids are rich in silicates, as the sodium bicarbonate crystals formed at step b) will catch most of the silica present in the stream (C), and this may improve the flowability of crystals (F).

60 In a preferred embodiment, the sodium carbonate bearing stream (A) is an aqueous solution (A') comprising sodium carbonate. In a more preferred embodiment, the aqueous solution (A') is a purge from a sodium carbonate crystallizer. And in a most preferred embodiment, the aqueous solution (A') is a purge from a sodium carbonate monohydrate crystallizer. In a variant of this most preferred embodiment the

aqueous solution (A') is a purge from a sodium carbonate monohydrate crystallizer in combination with tailings pond solids deriving from sodium carbonate crystallizers purges.

In another variant of this most preferred embodiment, the process of the present invention is coupled with the process described in WO2011/138005A1 (Solvay Chemicals), which is incorporated herewith by reference. In this case the process of the present invention further comprises:

k) depositing the remainder (I) of the stream (B) in a tailings pond, wherein part of the remaining sodium carbonate in the tailings pond crystallizes into a solid mass comprising sodium carbonate decahydrate and wherein a concentrated solution (Q) is formed comprising impurities selected from the group consisting of silicates, sodium chloride, sodium sulfate, organic matter, and combinations of two or more thereof;

l) optionally contacting said solid mass with a leach solution to selectively dissolve at least a portion of a first impurity from the contacted mass into the leach solution to form a leachate and a leached residue, collecting the leached residue, dissolving at least a portion of the leached residue in an aqueous medium to form a liquor; optionally carrying out a second impurity removal step comprising performing a magnesium treatment to form a treated liquor, said treatment comprising adding a magnesium compound during dissolution of the leached residue or adding a magnesium compound to said liquor or a portion thereof after dissolution of the leached residue in order to form water-insoluble matter with at least a portion of a second impurity, and passing said treated liquor through at least one separation unit to remove water-insoluble matter and to obtain a purified solution; and

m) providing said solid mass or said liquor or said purified solution as a feedstock to a process which produces a crystalline product comprising sodium carbonate, sodium bicarbonate, sodium sulfite, or other derivatives.

The remainder (I) of the stream (B) or a part (J) of the mother liquor (G) is concentrated in water-soluble salts and other impurities present in the sodium carbonate bearing stream (A). Therefore in another variant of the present invention, the process further comprises at least one of the following steps:

n) disposing of the remainder (I) of the stream (B) or a part (J) of the mother liquor (G) in a solution mining cavity or a mined out cavity or in a deep well injection or,

o) recycling the remainder (I) of the stream (B) or a part (J) of the mother liquor (G) or a part (L) of the liquor (K) in a solution mining cavity or a mined out cavity, and recovering a sodium carbonate aqueous solution from the solution mining cavity or from the mined out cavity, wherein the recovered sodium carbonate aqueous solution comprises sodium chloride and/or sodium sulfate at a sodium chloride and/or sodium sulfate concentration less than the concentration of sodium chloride and/or the concentration of sodium sulfate in the remainder (I) or the part (J) or the part (L).

Steps n) or o) are particularly advantageous when the sodium carbonate bearing stream (A) derives, in part or in its entirety, from trona or nahcolite, as it enables to recycle the water-soluble salts that were originally present in the ore within the mine cavity, the mine or the deep well. Moreover, the pH of the final purges may be controlled by way of the sodium bicarbonate content, as sodium bicarbonate is a natural pH buffer. Thus the volume that is recycled in such cavity or mine, or deep well, is much reduced compared to the volume of the original ore extracted from the cavity or from the mine, or from the deep well.

Generally, the sodium carbonate bearing stream (A) comprises at least 15 weight percent of sodium carbonate expressed on dry soluble salts. Advantageously, stream (A) comprises at least 20, more advantageously at least 24 weight percent of sodium carbonate expressed on dry soluble salts.

The stream (A) is advantageously selected from the group consisting of recycle and purge streams from sodium carbonate or sesquicarbonate crystallizers, mine water streams, evaporative pond bittern aqueous streams, water and sodium carbonate decahydrate deposits, other waste streams, and any combinations thereof.

Stream (A) comprises generally at most 98, advantageously at most 95, more advantageously at most 85 weight percent of sodium carbonate expressed on dry soluble salts. When the sodium carbonate bearing stream (A) is a suspension of a solid in an aqueous solution, or an aqueous solution, it comprises generally at most 99, advantageously at most 90, more advantageously at most 80 weight percent of water. This enables to limit the number of recycling in the sodium bicarbonate loop of the present invention.

If the sodium carbonate stream derives from a solid stream, or is an aqueous suspension, or an aqueous solution concentrated in sodium carbonate, water (N) may be added to the sodium carbonate bearing stream (A) so that the combination of the stream (B) with stream (A) forms a feeding stream (C) suitable to form crystals (F) comprising sodium bicarbonate crystals when bicarbonated. In particular, the amount of water (N) is controlled in order to limit the density of suspension of crystals (F) in the aqueous suspension (E) to generally at most 60 w %, advantageously at most 50 w %, preferably at most 40 w %, more preferably at most 35 w %. The density of suspension of solids in an aqueous suspension being the weight ratio of the solid reported to the aqueous suspension.

In the present invention, the stream (A) comprises at least 2%, advantageously at least 3%, more advantageously at least 4% sodium chloride and/or sodium sulfate by weight.

The stream (A) may contain high level of sodium chloride and/or sodium sulfate. Though advantageously, the concentration of stream (A) in sodium chloride and/or sodium sulfate should be limited to a maximum value so that the stream (G), corresponding to the mother liquor of the bicarbonate crystallizer separated at step c), has a concentration of at most 26% (260 g/kg) in sodium chloride or at most 20% (200 g/kg) in sodium sulfate by weight in order to avoid reaching the limit of water-solubility of sodium chloride and/or sodium sulfate in stream (G). In the case that stream (A) comprises both sodium chloride and sodium sulfate, those two impurities concentration in stream (G), noted respectively [NaCl] (G) and [Na₂SO₄](G) and expressed in g/kg, should be advantageously limited according the following equation:

$$[\text{NaCl}](\text{G})/1.3 + [\text{Na}_2\text{SO}_4](\text{G}) \leq 200 \text{ g/kg}$$

Also when significant concentration of other highly water-soluble salts with common ion with sodium, or chloride, or sulfate ions, in a proportion when cumulated of at least 5% in weight of the cumulated sodium chloride and sodium sulfate amount of stream (A), those impurities salt concentrations should be added to the sum of the concentrations of sodium chloride and sodium sulfate, and this later sum should preferably be maintained to at most 20% (200 g/kg) by weight in stream (G).

In the present invention, the streams (I) or (J) (or (L)) are used to control the alkaline metal water-soluble salt concentration, such as sodium chloride, or sodium sulfate concentrations, in the aqueous mother liquor (G) during bicarbonation step b). When the flow of streams (I) or (J) (or (L)) increase, the concentration of the alkaline metal water-

soluble salt(s) concentration(s) $C_i(G)$ in the process loop decreases, and vice versa. Those flows may be adjusted so that at the targeted concentration of the alkaline metal water-soluble salt in the aqueous mother liquor (G) or in the streams (I) or (J) (or (L)), the flows of purged alkaline metal water-soluble salt in the corresponding streams (I) or (J) or (L)) equal the entering flow of the alkaline metal water-soluble salt entering in the process (i.e., via streams (A), (A'), (A'') and (A''')) minus the flow of the alkaline metal water-soluble salt exiting the process with the crystals (F).

Generally, when the stream (A) is the aqueous purge of a monohydrate crystallizer, the NaCl concentration of the purge is at most 5% and the Na_2SO_4 concentration of the purge is at most 7% expressed on the aqueous solution in weight. Indeed a classical MVR (Mechanical Vapor Recompression) crystallizer cannot operate at NaCl levels significantly higher than 2-3% without crystallizing anhydrous sodium carbonate, which causes operational difficulties. Triple effects monohydrate evaporator crystallizer is operated at lower temperatures and can accept higher concentrations of NaCl, up to 4-5% depending on a number of factors. A Na_2SO_4 concentration above 3 to 7% induces burkeite crystals ($\text{Na}_2\text{CO}_3 \cdot 2\text{Na}_2\text{SO}_4$) formation at the crystallizer temperature (between 40° to 100° C.).

Typical natural soda ash plant from trona have a Na_2CO_3 feed concentration in the liquor of 28 to 30% by weight, NaCl feed concentration of about 0.2%, and/or Na_2SO_4 feed concentration of about 0.05 to 0.2%, meaning that a traditional plant in the prior art comprising a sodium carbonate crystallizer can operate between 10 and 20 cycles of concentration. This number of cycle of concentrations is generally close to the ratio of the final concentration to the feeding concentration of the water-soluble impurity. This is what ultimately imposes product loss, purge volumes, and the size of ponds and disposals in a natural soda ash plant without recovery of the valuable alkali. The present invention enables to sensitively increase the number of cycles of concentrations from 10 to 20 cycles up to 75 cycles, and even more in a simple way. Moreover, the present process enables to limit the energy consumption and related costs reported to the total sodium carbonate production, when the sodium carbonate stream (A) is a purge of a sodium carbonate crystallizer, as the purge represents generally from 2 to 15% of the sodium carbonate flow entering the sodium carbonate crystallizer.

In present invention, the partly debicarbonating of the aqueous mother liquor (G) and the removing of part of the water at step d) may be done by any mean known in the art. The partly debicarbonating and removing of part of the water may be done in one step or in several steps. Generally the debicarbonating is done by chemical calcination using caustic soda to transform part of the sodium bicarbonate of liquor (G) into sodium carbonate, or done by thermal debicarbonation using steam or using a boiler to decompose thermally part of sodium bicarbonate into sodium carbonate, water and CO_2 . Thermal debicarbonation using steam or a boiler is preferred. The removing of part of the water of liquor (G) may be done in a falling film evaporator, or in a boiler, or in a forced circulation evaporator, or in a forced circulation evaporator crystallizer known in the art.

The process according to an embodiment of the invention using a thermal debicarbonator at step d) is illustrated in FIG. 1 (FIG. 1). The sodium carbonate bearing stream (A) is mixed with part of a stream (B) to produce a stream (C). The stream (C) is bicarbonated with a gas (D) comprising CO_2 in a carbonating device 1 to produce an aqueous suspension (E) comprising crystals (F), said crystals (F) comprising sodium bicarbonate crystals. The suspension (E) is separated into

crystals (F) comprising sodium bicarbonate crystals on the one hand and an aqueous mother liquor (G) on the other hand with a separation device 2. The aqueous mother liquor (G) is partly debicarbonated and part of the water is removed to obtain the stream (B) and an optional gas (H) comprising CO_2 in a debicarbonator 3. Therefore the stream (B) is more concentrated in water-soluble salt content than the stream (G). At least part of the stream (B) is recycled to form the stream (C) when it is combined with stream (A). The remainder (I) of the stream (B) is removed from the loop (which includes the devices 1, 2, 3) or a part (J) of the aqueous mother liquor (G) is removed to be further processed.

FIG. 2 is a flow diagram of a process according to an embodiment of the present invention. In this embodiment, the debicarbonation and the removal of part of the water of stream (G) is done into two steps, and optional water and CO_2 gas (H) recyclings are shown in dotted lines. In this embodiment, the sodium carbonate bearing stream (A) may be mixed with optional water (N) to form an aqueous solution (A') comprising sodium carbonate, and mixed with a stream (B) to produce a stream (C). The stream (C) is bicarbonated with a gas (D) comprising CO_2 in a carbonating device 1 to produce an aqueous suspension (E) comprising crystals (F), said crystals (F) comprising sodium bicarbonate crystals. The suspension (E) is separated into crystals (F) comprising sodium bicarbonate crystals on the one hand and an aqueous mother liquor (G) on the other hand with a separation device 2. The aqueous mother liquor (G) is debicarbonated in a debicarbonator 3 to produce a mother liquor (K) depleted or lean in sodium bicarbonate and a vapor (H) comprising carbon dioxide, and the mother liquor (K) is partially evaporated to remove part of the water in an evaporator 4 to obtain the stream (B) and the water steam (P). The stream (B) may be a clear liquid or a slurry. Optionally, a portion of or the entirety of the water steam (P) may be recycled to the debicarbonator 3 and injected directly or after recompression of steam or may be recycled to the debicarbonator 3 as indirect heating by a boiler. At least part of the stream (B) is recycled to form stream (C) when it is combined with stream (A). The remainder (I) of the stream (B) is withdrawn from the loop, and/or a part (J) of the aqueous mother liquor (G) is withdrawn from the loop, and/or a part (L) of the mother liquor (K) is withdrawn from the loop to be further processed. Those streams (I), (J), (L) are indeed useful to control the water-soluble salt concentrations, such as sodium chloride, or sodium sulfate concentrations, in the aqueous mother liquor during bicarbonation step b) in the bicarbonator 1.

In a variant of this embodiment, a sodium carbonate bearing stream (A''), such as one or more mine waters, or tailings pond waters, or diluted waters, may be added to the mother liquor (K) depleted or lean in sodium bicarbonate before partially evaporating it to remove part of the water so as to obtain the stream (B). This allows to advantageously avoid the limit of water-solubility of sodium carbonate and/or sodium chloride or sodium sulfate in the evaporator 4.

In another variant of this embodiment, if a sodium carbonate bearing stream (A''') such as one or more mine waters, tailings pond waters, or diluted waters, have a sodium bicarbonate content, or a water content and a sodium bicarbonate content, to be first decreased before being recycled in the bicarbonator 1, an adequate point to introduce this stream A''' in the process is in the debicarbonator 3 with the aqueous mother liquor G.

Optionally, in present invention, at step d), the optional gas (H) is produced, and at least a portion of said gas (H) is used with the gas (D) for bicarbonating the stream (C). In the embodiment illustrated in FIG. 2, at least a portion of the gas

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(H) is used for bicarbonating the stream (C) with the gas (D). Indeed, the gas (H) comprises a high content of CO₂ and the remainder of its content is mainly steam (water vapor) that may be reused at step b), without water condensation or with water condensation and water removal, before being introduced in stream (D) to control the water balance of the present process with the water removal via withdrawal of stream (I), (L), (J) and (P) from the loop.

In the present process, at step b), the gas (D) is a gas comprising at least 20, advantageously at least 30, more advantageously at least 40, even more advantageously at least 80 volume % CO₂ expressed on dry gas.

The bicarbonation step b) is operated at any temperature compatible with known domain of sodium bicarbonate. Preferably, the bicarbonation step b) is operated at a temperature of at least 20° C., advantageously at least 38° C., more advantageously at least 55° C., and even more advantageously at least 70° C.

A too high temperature may be detrimental to CO₂ absorption when not operated at pressure above atmospheric pressure. Therefore, the bicarbonation step b) is generally operated at a temperature of at most 100° C., advantageously at most 90° C., more advantageously at most 80° C., and even more advantageously at most 75° C.

In the present invention, the crystals (F) obtained at step b) comprise sodium bicarbonate crystals. Advantageously, the operating point (mother liquor concentrations of sodium bicarbonate, of sodium carbonate, and of soluble salts such as NaCl and Na₂SO₄) in the carbonation step should be controlled so that it remains in the sodium bicarbonate domain of the water solubility diagram. This is achieved supplying enough CO₂ in the bicarbonator so that the sodium carbonate concentration in the bicarbonator mother liquor (G) is less than the limit of sodium carbonate concentration at the sodium sesquicarbonate solubility noted [Na₂CO₃](sesqui) at the operating temperature.

If [X](G) represents the soluble salt concentrations expressed in g/kg of NaCl, or of Na₂SO₄, or the sum of NaCl and Na₂SO₄ concentrations if both salts are present, this is generally achieved between 20° to 80° C., when the sodium carbonate concentration of the mother liquor (G), noted [Na₂CO₃](G), is less than the following value (expressed in g/kg):

$$170 - 0.66[X](G) \text{ (g/kg)}$$

A security margin should be taken so that the sodium carbonate concentration is preferably at most this value minus 5 g/kg, more preferably at most this value minus 10 g/kg, and most preferably at most this value minus 20 g/kg.

This allows the crystallization of mainly sodium bicarbonate. Then if the corresponding crystals (F) are separated from their mother liquor (G) which is concentrated in NaCl and/or Na₂SO₄, and if optionally the obtained crystals are washed when necessary to remove high levels of impregnating mother liquor and water-soluble salts such as NaCl or Na₂SO₄, the content of crystals (F) comprising sodium bicarbonate crystals is generally at least 40 wt %, or at least 50 wt %, preferably at least 60 wt %, more preferably at least 80 wt %, and most preferably at least 90 wt % of sodium bicarbonate. The crystals (F) comprises generally at most 50 wt %, or at most 30 wt %, or at most 20 wt %, preferably at most 10 wt %, more preferably at most 5 wt %, and most preferably at most 3 wt % of sodium carbonate.

The content of the crystals (F) in water-soluble salts such as sodium chloride and/or sodium sulfate is generally at most 10 wt. %, preferably at most 4 wt. %, more preferably at most 1 wt. %.

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Concerning the final use of the obtained crystals (F) comprising sodium bicarbonate, the process of the present invention may further comprise:

- g) optionally washing the crystals (F) comprising sodium bicarbonate to produce optionally-washed crystals comprising sodium bicarbonate,
- h) drying the optionally-washed crystals comprising sodium bicarbonate.

Alternatively, it is possible to calcine, in part or partly or totally the sodium bicarbonate rather than solely drying the crystals in step h).

In that case, the process according the present invention further comprises the steps of:

- g) optionally washing the sodium bicarbonate crystals to produce optionally-washed crystals comprising sodium bicarbonate, and
- i) calcining the optionally-washed crystals comprising sodium bicarbonate into crystals comprising sodium carbonate.

When calcining, partly or totally, the sodium bicarbonate of the crystals at step i), a gas (O) comprising carbon dioxide is generated. The carbon dioxide and the water can be, totally or partly, recovered and recycled to the bicarbonation step.

Therefore the process of the present invention may further comprise the step:

- j) recovering at least part of the gas (O) comprising carbon dioxide and recycling it to step b).

EXAMPLES

The following examples are intended only to exemplify the invention and are not intended to limit the scope of the claimed invention.

Example 1

TABLE 2 exemplifies a mass flowsheet of an embodiment of the process of the present invention as described in FIG. 2, wherein the main water-soluble salt impurity of the sodium carbonate stream (A) is sodium chloride.

This example shows the strong interest in the case where the sodium carbonate stream (A) is a purge from a sodium carbonate crystallizer; the mass flow rate of the final purge (I) is 226 kg/h, such value representing less than a quarter of the value of the original purge (A) at 1000 kg/h, and the loss of sodium carbonate from the final purge (I) is 27 kg/h so a reduction in mass by a factor of almost 9 compared to the initial value of 242 kg/h of sodium carbonate in the initial purge (A), thanks to the recycling loop associated with a debicarbonator and an evaporator of the present process.

By comparison, US2009/0291038 (Solvay) shows in its Example 1 a decrease of sodium alkali loss in the final purge of 60%, compared to about 90% in present Example 1, and a reduction of 10% of the mass flow rate of the initial purge compared to about 77% in the present Example 1.

Example 2

In this example, the same data of TABLE 2 can illustrate a mass flow rate sheet of an embodiment of the process of the present invention as described in FIG. 2, wherein the main water-soluble salt impurity of the sodium carbonate stream (A) is sodium sulfate (Na₂SO₄). In this case, sodium chloride (NaCl) mass flow rate and sodium chloride (NaCl) concentrations should be respectively interpreted as Na₂SO₄ mass flow rates and Na₂SO₄ concentrations rather than those of NaCl.

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Example 3 to 7

E0 to E6

In these examples, similar equipment and operating conditions as those used in Example 1 of US2009/0291038 (Solvay) were used but the bicarbonation was operated in batch, in an agitated 3-liter reactor, at 70° C., with CO₂ gas at 100% vol. dry concentration and saturated with water, with one hour of residence time.

The obtained crystals were filtered, washed with water and ethanol, and dried for 24 hours at ambient temperature.

TABLE 3 gives the results of the analysis of initial and final mother liquors, of the obtained crystals, the density of suspension (solid weight reported to the suspension weight) and also of particles size distribution of the obtained crystals.

Should the disclosure of any patent, patent applications, and publications that are incorporated herein by reference conflict with the present description to the extent that it might render a term unclear, the present description shall take precedence.

TABLE 2

Example 1 - Mass Balance flowsheet.												
Stream	(A) = (A')	(A'')	(B)	(C)	(D)	(E)	(F)	(G)	(H)	(I)	(K)	(O) If calcined
Phase	liquid	liquid	liquid	liquid	gas	slurry	solid	liquid	gas	liquid	liquid	gas
Flow rate (kg/h)	1000	500	1477	1751	94	1845	345	1500	28	226	1472	127
Liquid												
NaHCO ₃	7	7	56	54		68		68		9	50	
Na ₂ CO ₃	121	121	176	270		44		44		27	55	
NaCl	20	20	255	236		236		236		39	236	
H ₂ O	353	353	990	1192		1154		1154		151	1132	
Total Liquid	500	500	1477	1751		1500		1500		226	1472	
Mass fraction (g/kg)												
NaHCO ₃	13	13	38	31		45		45		38		
Na ₂ CO ₃	242	242	119	154		29		29		119		
NaCl	39	39	173	134		157		157		173		
H ₂ O	706	706	670	681		769		769		670		
Solid												
Flow rate (kg/h)												
NaHCO ₃						345	345					
Na ₂ CO ₃						0	0					
Total Solid						345	345					
Gas												
Flow (kg/h)												
H ₂ O					0				23			37
CO ₂					94				5			90
Total Gas					94				28			127

TABLE 3

Operating conditions, and chemical and physical analysis of the obtained crystals of Examples 3 to 7 (respectively referenced E0, E2, E3, E6).					
Ref. Trial	#	E0	E2	E3	E6
Temperature	° C.	70	70	70	70
Residence time	h	1	1	1	1
Initial mother liquor					
NaHCO ₃	g/kg	79	54	44	45
Na ₂ CO ₃	g/kg	49	52	52	50
NaCl	g/kg	136	144	153	75
Na ₂ SO ₄	g/kg	—	—	—	75
H ₂ O	g/kg	736	750	751	755
Total	g/kg	1000	1000	1000	1000

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TABLE 3-continued

Operating conditions, and chemical and physical analysis of the obtained crystals of Examples 3 to 7 (respectively referenced E0, E2, E3, E6).					
Ref. Trial	#	E0	E2	E3	E6
Final mother liquor					
NaHCO ₃	g/kg	50	48	45	62
Na ₂ CO ₃	g/kg	11	20	10	17
NaCl	g/kg	146	153	165	78
Na ₂ SO ₄	g/kg	—	—	—	77
H ₂ O	g/kg	793	779	780	766
Total	g/kg	1000	1000	1000	1000
Final dried solid					
NaHCO ₃	g/kg	942	915	908	906
Na ₂ CO ₃	g/kg	29	38	41	38
NaCl	g/kg	9	30	42	8

TABLE 3-continued

Operating conditions, and chemical and physical analysis of the obtained crystals of Examples 3 to 7 (respectively referenced E0, E2, E3, E6).					
Ref. Trial	#	E0	E2	E3	E6
Na ₂ SO ₄	g/kg	—	—	—	8
H ₂ O	g/kg	20	17	9	40
Suspension density	w %	6.9	6.3	6.5	4.7
Particle size distri.					
d10	μm	121	41	39	50
d50	μm	376	129	125	126
d90	μm	678	280	415	566

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The invention claimed is:

1. A process for producing sodium bicarbonate from a sodium carbonate bearing stream (A), a part of which is generated by a sodium carbonate crystallizer, said sodium carbonate bearing stream (A) comprising sodium carbonate and at least 2% sodium chloride and/or sodium sulfate by weight, said process comprising the following steps:

- a) mixing the sodium carbonate bearing stream (A) with at least a part of a stream (B) to produce a stream (C);
- b) bicarbonating the stream (C) with a gas (D) comprising CO₂ to produce an aqueous suspension (E) comprising crystals (F), said crystals (F) comprising sodium bicarbonate crystals;
- c) separating the aqueous suspension (E) in order to obtain crystals (F) comprising sodium bicarbonate crystals and an aqueous mother liquor (G);
- d) partly debicarbonating the aqueous mother liquor (G) and removing part of the water to obtain the stream (B) and an optional gas (H);
- e) recycling at least a part of the stream (B) to step a); and
- f) removing a remainder (I) of the stream (B) which is not recycled to step (a) or a part (J) of the aqueous mother liquor (G) which is not partly debicarbonated in step d) to be further processed.

2. The process of claim 1, wherein the sodium carbonate crystallizer is selected from the group consisting of: an anhydrous sodium carbonate crystallizer, a sodium carbonate monohydrate crystallizer, a sodium carbonate heptahydrate crystallizer, a sodium carbonate decahydrate crystallizer, a sodium carbonate sesquicarbonate crystallizer, a wegscheiderite crystallizer, and any combination thereof.

3. The process according to claim 1, wherein the sodium carbonate from the sodium carbonate bearing stream (A) is derived, partly or totally, from trona.

4. The process of claim 3, wherein the sodium carbonate from the sodium carbonate bearing stream (A) is derived, partly or totally, from trona processed by conventional mining.

5. The process according to claim 3, wherein the sodium carbonate from the sodium carbonate bearing stream (A) is derived, partly or totally, from trona processed by solution mining.

6. The process according to claim 1, wherein the sodium carbonate bearing stream (A) is derived, partly or totally, from tailings pond solids comprising sodium carbonate.

7. The process according to claim 1, wherein the sodium carbonate bearing stream (A) is an aqueous solution (A') comprising sodium carbonate.

8. The process of claim 7, wherein the aqueous solution (A') is a purge from a sodium carbonate monohydrate crystallizer.

9. The process according to claim 1, wherein at step d), the optional gas (H) is a gas comprising at least 20 volume % CO₂ expressed as dry gas.

10. The process according to claim 1, wherein at step d), the optional gas (H) is produced, and wherein at least a portion of said gas (H) is used with the gas (D) for bicarbonating the stream (C).

11. The process according to claim 1, wherein the step b) is operated at a temperature of at least 20° C.

12. The process according to claim 1, further comprising:
- g) optionally washing the crystals (F) comprising sodium bicarbonate to produce optionally-washed crystals comprising sodium bicarbonate, and
 - h) drying the optionally-washed sodium bicarbonate crystals.

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13. The process according to claim 1, further comprising:

- g) optionally washing the crystals (F) comprising sodium bicarbonate crystals to produce optionally washed crystals comprising sodium bicarbonate, and

- i) calcining the optionally-washed crystals comprising sodium bicarbonate into crystals comprising sodium carbonate.

14. The process according to claim 13, wherein a gas (O) comprising carbon dioxide is generated during the calcination step i); and

wherein the process further comprises:

- j) recovering at least a part of the gas (O) comprising carbon dioxide and recycling it to step b).

15. The process according to claim 1, wherein, at step d), the aqueous mother liquor (G) is debicarbonated in a debicarbonator to produce a mother liquor (K) depleted or lean in sodium bicarbonate and a vapor (H) comprising carbon dioxide, and

wherein the mother liquor (K) depleted or lean in sodium bicarbonate is partially evaporated to remove part of the water so as to obtain the stream (B), optionally further comprising recycling at least part of the vapor (H) comprising carbon dioxide at step b).

16. The process according to claim 15, further comprising adding a sodium carbonate bearing stream (A") to the mother liquor (K) depleted in sodium bicarbonate before partially evaporating said mother liquor to remove part of the water to obtain the stream (B).

17. The process according to claim 1, further comprising: depositing the remainder (I) of the stream (B) in a tailings pond, wherein part of remaining sodium carbonate in the tailings pond crystallizes into a solid mass comprising sodium carbonate decahydrate and wherein a concentrated solution (Q) is formed comprising impurities selected from the group consisting of silicates, sodium chloride, sodium sulfate, organic matter, and combinations of two or more thereof;

optionally contacting said solid mass with a leach solution to selectively dissolve at least a portion of a first impurity from the contacted mass into the leach solution to form a leachate and a leached residue, collecting the leached residue, dissolving at least a portion of the leached residue in an aqueous medium to form a liquor; optionally carrying out a second impurity removal step comprising performing a magnesium treatment to form a treated liquor, said treatment comprising adding a magnesium compound during dissolution of the leached residue or adding a magnesium compound to said liquor or a portion thereof after dissolution of the leached residue in order to form water-insoluble matter with at least a portion of a second impurity, and passing said treated liquor through at least one separation unit to remove water-insoluble matter and to obtain a purified solution; and providing said solid mass or said liquor or said purified solution as a feedstock to a process which produces a crystalline product comprising sodium carbonate, sodium bicarbonate, or sodium sulfite.

18. The process according to claim 1, further comprising: disposing of the remainder (I) of the stream (B) or the part (J) of the mother liquor (G) or a part (L) of a liquor (K) produced when said aqueous mother liquor (G) is debicarbonated, in a solution mining cavity or a mined out cavity or in a deep well injection.

19. The process according to claim 1, further comprising: recycling the remainder (I) of the stream (B) or the part (J) of the mother liquor (G) or a part (L) of a liquor (K) produced when said aqueous mother liquor (G) is debi-

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carbonated, in a solution mining cavity or a mined out cavity, and recovering a sodium carbonate aqueous solution from the solution mining cavity or from the mined out cavity, wherein the recovered sodium carbonate aqueous solution comprises sodium chloride and/or sodium sulfate at a sodium chloride and/or sodium sulfate concentration less than the concentration of sodium chloride and/or the concentration of sodium sulfate in the remainder (I) or the part (J) or the part (L).

20. A process for joint production of sodium carbonate and bicarbonate crystals, comprising:

in a first step introducing a sodium carbonate solution comprising sodium carbonate and at least one impurity consisting of sodium chloride and/or sodium sulfate into a sodium carbonate crystallizer;

producing a first aqueous suspension comprising sodium carbonate crystals; and

subjecting the first aqueous suspension to a separation, in order to obtain crystals comprising sodium carbonate which are valorized, and a mother liquor,

wherein a part of the mother liquor is taken out of the sodium carbonate crystallizer to constitute the sodium carbonate bearing stream (A) to be further processed according to the process for producing sodium bicarbonate of claim 1.

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